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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup>:

A61K 7/06

A2

(11) International Publication Number: WO 98/40046

(43) International Publication Date: 17 September 1998 (17.09.98)

(21) International Application Number: PCT/US97/03564

(22) International Filing Date: 10 March 1997 (10.03.97)

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

#### **Published**

Without international search report and to be republished upon receipt of that report.

(54) Title: HAIR CONDITIONING COMPOSITIONS

#### (57) Abstract

Disclosed are hair conditioning compositions comprising by weight: (a) from about 0.4 % to about 5.0 % of an amidoamine; (b) from about 0.05 % to about 2.0 % of an acid; (c) from about 1 % to about 15 % of a high melting point compound having a melting point of at least about 25° C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof; (d) from about 0.02 % to about 2 % of an oily compound having a melting point of not more than about 25° C selected from the group consisting of a first oily compound, a second oily compound, and mixtures thereof; and (e) water; wherein the molar ratio of the amidoamine to acid is about 1: 0.3 to about 1: 1, and wherein the composition is substantially free of quaternary ammonium compounds. Further disclosed are suitable methods of making the conditioning compositions.

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#### HAIR CONDITIONING COMPOSITIONS

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#### **TECHNICAL FIELD**

The present invention relates to hair conditioning compositions free of quaternary ammonium compounds. More specifically, the present invention relates to a hair conditioning composition comprising an amidoamine, an acid, a high melting point compound, an oily compound, and water.

#### BACKGROUND

Scalp and hair become soiled due to their contact with the surrounding environment and from sebum secreted from the hair follicles. The build-up of sebum and environmental soiling can cause the hair to have a dirty or greasy feel, and an unattractive appearance. In order to ameliorate these effects, it is necessary to shampoo the hair with regularity.

Shampooing the hair removes excess sebum and other environmental soiling but has disadvantages in that the hair can be left in a wet, tangled, and relatively unmanageable state. Shampooing can also result in the hair becoming dry due to the removal of natural oils or other hair moisturizing materials. After shampooing, the hair can also suffer from a perceived loss of "softness." Frequent shampooing also contributes to the phenomena of "split ends," particularly for long hair. Split ends refers to a condition wherein the ends of the hair are split into two or more shafts, resulting in a frizzy appearance.

A variety of approaches have been developed to condition the hair. These range from post-shampooing hair rinses, to leave-on hair conditioners, to the inclusion of hair conditioning components in shampoos. Although many consumers prefer the ease and convenience of a shampoo which includes conditioners, a substantial proportion of consumers prefer the more conventional conditioner formulations which are applied to the hair as a separate step from shampooing, usually subsequent to shampooing. These hair conditioners typically are formulated as a thickened product, such as a gel or cr am, for ease of dispensing and application to the hair.

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Hair conditioning compositions have conventionally been based on the combination of a cationic surfactant, which is generally a quaternary ammonium compound such as ditallowdimethylammoniumchloride, in combination with various conditioning agents such as amidoamines, fatty alcohols, or oily compounds. These combinations generally result in a gel-network structur which provides the compositions with a thick, creamy texture. However, quaternary ammonium compounds may cause harshness and irritation to scalp, hair and/or skin. Further, some of the quaternary ammonium compounds such as ditallowdimethylammonium chloride are not biodegradable, and consequently are not preferred in view of environmental requirements.

In addition, consumers tend to prefer conditioners which provide certain feel to the wet hair such as ease of spreading and ease of rinsing, as well as to the dry hair such as hair smoothness and softness, lustery appearance, and easy combing.

Use of amidoamines in conditioning compositions are known in the art, such as in Japanese Patent Laid-open No. H5-271035, H5-271036, and H7-2629. Use of oily compounds in conditioning compositions such as low melting point fatty alcohols are also known in the art.

Based on the foregoing, there is a need for a hair conditioning composition which is substantially free of quaternary ammonium compounds, while continuing to provide preferable conditioning benefits. None of the existing art provides all of the advantages and benefits of the present invention.

#### SUMMARY

The present invention is directed to a hair conditioning composition comprising by weight: (a) from about 0.4% to about 5.0% of an amidoamine; (b) from about 0.05% to about 2.0% of an acid; (c) from about 1% to about 15% of a high melting point compound having a melting point of at least about 25°C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof; (d) from about 0.02% to about 2% of an oily compound having a melting point of not more than about 25°C selected from the group consisting of a first oily compound, a second oily compound, and mixtures thereof; and (e) water; wherein the molar ratio of the amidoamine to acid is from about 1: 0.3 to about 1: 1, wherein the composition is substantially free of quaternary ammonium compounds.

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The present invention is further directed to a suitable process for providing the hair conditioning composition.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

#### **DETAILED DESCRIPTION**

While the specification concludes with claims particularly pointing and distinctly claiming the invention, it is believed the present invention will be better understood from the following description.

All percentages are by weight of the total composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. All percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined as commercially available products, unless otherwise indicated.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

#### **AMIDOAMINE**

The compositions of the present invention comprise by weight from about 0.4% to about 5.0%, preferably from about 1.0% to about 3.0% of an amidoamine having the following general formula:

 $R^{1}$  CONH (CH<sub>2</sub>)<sub>m</sub> N ( $R^{2}$ )<sub>2</sub>

wherein R<sup>1</sup> is a fatty acid residue having from about 11 to about 24 carbon atoms, R<sup>2</sup> is an alkyl having from 1 to about 4 carbon atoms, and m is an integer from 1 to about 4.

Preferred amidoamines stearamidopropyldimethylamine, stearamidoethyldiethylamine, palmitamidopropyldimethylamine, palmitamidoethyldi thylamine, behenamidopropyldimethylamine,

useful herein include stearamidopropyldiethylamine, stearamidoethyldimethylamine, palmitamidopropyldiethylamine, palmitamidoethyldimethylamine, behenamidopropyldiethylamine,

behenamidoethyldiethylamine, arachidamidopropyldimethylamine, arachidamidopropyldiethylamine, arachidamidoethyldiethylamine, arachidamidoethyldimethylamine, and mixtures thereof; more preferably stearamidopropyldimethylamine, and mixtures thereof.

Commercially available amidoamines useful herein include: stearamidopropyldimethylamine with tradenames LEXAMINE S-13 available from Inolex (Philadelphia Pennsylvania, USA) and AMIDOAMINE MSP available from Nikko (Tokyo, Japan), stearamidoethyldiethylamine with a tradename AMIDOAMINE S available from Nikko, behenamidopropyldimethylamine with a tradename INCROMINE BB available from Croda (North Humberside, England), and various amidoamines with tradenames SCHERCODINE series available from Scher (Clifton New Jersey, USA).

**ACID** 

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The compositions of the present invention comprise by weight from about 0.05% to about 2.0%, preferably from about 0.2% to about 1.5%, and more preferably from about 0.3% to about 1.0%, of an acid. The acid is also included at such a level to provide a molar ratio of the amidoamine to the acid of from about 1:0.3 to about 1:1, preferably from about 1:0.5 to about 1:0.9.

The acid useful herein can be any used by those skilled in the art, including organic acids and inorganic acids. Nonlimiting examples of acids include L-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, L-glutamic acid hydrochloride, tartaric acid, and mixtures thereof; preferably L-glutamic acid, lactic acid, hydrochloric acid, and mixtures thereof.

Commercially available acids useful herein are those having the same tradenames as their compound names including: L-GLUTAMIC ACID (cosmetic grade) available from Ajinomoto (Tokyo, Japan), CITRIC ACID (USP) available from Roche (Nutley New Jersey, USA), ANHYDROUS CITRIC ACID available from Harrmann & Reimer (Springfield New Jersey, USA), MALIC ACID available from Kyowa Hakko (Tokyo, Japan) and Fuso Kagaku (Osaka, Japan), and lactic acid with a tradename UNICHEM LACA available from UPI.

#### HIGH MELTING POINT COMPOUND

Th compositions of the present invention comprise by weight from about 1% to about 15%, preferably from about 1.4% to about 10%, more preferably

from about 3% to about 8% of a high melting point compound having a melting point of at least about 25°C selected from the group consisting of fatty alcohols. fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof. Without being bound by theory, it is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of combing. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than about 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

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The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds

having esterifiable hydroxy groups, hydroxy-substitued fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; ceteareth 1 through ceteareth-10, which are the ethylene glycol ethers of ceteareth alcohol, i.e. a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C1-C30 alkyl ethers of the ceteth, steareth, and ceteareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristate, polyoxyethylene myristyl cetyl ether polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene propyleneglycol distearate, monostearate. propyleneglycol trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By "pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point compounds useful herein include: cetyl alchol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from New Japan Chemical (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty

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acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

### 5 OILY COMPOUND

The compositions of the present invention comprise by weight from about 0.02% to about 2%, preferably from about 0.2% to about 1.5% of an oily compound having a melting point of not more than about 25°C selected from the group consisting of a first oily compound, a second oily compound, and mixtures thereof. The oily compounds useful herein may be volatile or nonvolatile. Without being bound by theory, it is believed that, the oily compounds may penetrate the hair to modify the hydroxy bonds of the hair, thereby resulting in providing softness and flexibility to the hair. The oily compound may comprise either the first oily compound or the second oily compound as described herein. Preferably, a mixture of the first oily compound and the second oily compound is used. The oily compounds of this section are to be distinguished from the high melting point compounds described above. Nonlimiting examples of the oily compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

#### First Oily Compound

The first oily compound may be included in the compositions of the present invention. Preferably the compositions of the present invention comprise by weight from about 0.1% to 0.75% of a first oily compound. The first oily compounds useful herein are selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, and mixtures thereof.

The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isocetyl alcohol, undecanol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol, decyl alcohol and lauryl alcohol.

The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

The fatty acid derivatives and fatty alcohol derivatives are defined herein to include, for example, esters of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, and mixtures thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol derivatives, include, for example, methyl linoleate, ethyl linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate, octyldodecyl isostearate, octyldodecyl isopalmitate, octyl isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, Oleth-2, pentaerythritol tetraoleate, pentaerythritol tetraisostearate, trimethylolpropane trioleate, and trimethylolpropane triisostearate.

Commercially available first oily compounds useful herein include: oleyl alcohol with tradename UNJECOL 90BHR available from New Japan Chemical, pentaerythritol tetraisostearate and trimethylolpropane triisostearate with tradenames KAKPTI and KAKTTI available from Kokyu Alcohol (Chiba, Japan), pentaerythritol tetraoleate having the same tradename as the compound name available from New Japan Chemical, trimethylolpropane trioleate with a tradename ENUJERUBU TP3SO available from New Japan Chemical, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl isostearate with a tradename HIS and isopropryl isostearate having a tradename ZPIS available from Kokyu Alcohol.

#### Second Oily Compound

The second oily compound may be included in the compositions of the present invention. Preferably the compositions of the present invention comprise by weight from about 0.1% to about 0.75% of a second oily compound. The second oily compounds useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, so long as they have a melting point of not more than about 25°C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from

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about 12 to about 30 carbon atoms, and preferably from about 12 to about 22 carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of  $C_{2-6}$  alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above. The branched chain polymers can have substantially higher chain lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are hydrocarbons selected from the group consisting of mineral oil, isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.

Commercially available second oily compounds useful herein include isododecane, isohexadeance, and isoeicosene with tradenames PERMETHYL 99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse (South Plainfield New Jersey, USA), a copolymer of isobutene and normal butene with tradenames INDOPOL H-100 available from Amoco Chemicals (Chicago Illinois, USA), mineral oil with tradename BENOL available from Witco, and isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas, USA).

#### 25 WATER

The compositions of the present invention comprise water for the remainder of the components described above, and other additional components as described hereinafter. Deionized water is preferably used. Water from natural sources including mineral cations can also be used, depending on the desired characteristic of the product.

## FREE OF QUATERNARY AMMONIUM COMPOUNDS

The compositions of the present invention are substantially free of quaternary ammonium compounds, which are commonly used in the art. Examples of quaternary ammonium compounds are those of the general formula:

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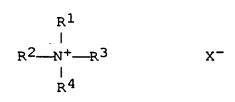
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wherein at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently an aliphatic group of from about 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 1 to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfate, and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups.

#### ADDITIONAL CONDITIONING AGENTS

The compositions of the present invention may further comprise additional conditioning agents. When included, additional conditioning agents are included at a level by weight of from about 0.1% to about 20.0%, preferably from about 1.0% to about 15.0%, and more preferably from about 2.0% to about 10% of the composition. Suitable conditioning agents are cationic polymers, silicones, proteins, and mixtures thereof.

# Cationic Polymers

Cationic polymers useful herein are those which are more or less water soluble. As used herein, the term "polymer" shall include materials whether made by polymerization of one type of monomer or made by two (i.e., copolymers) or more types of monomers. By "water soluble" cationic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. The preferred polymer will be sufficiently soluble to form a substantially clear solution at 0.5% concentration, more preferably at 1.0% concentration.

The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. Preferably, the molecular weight is from about

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100,000 to about 2 million. The cationic polymers will generally have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, and mixtures thereof.

The cationic charge density is preferably at least about 0.1 meq/gram, more preferably at least about 1.5 meq/gram, even more preferably at least about 1.1 meq/gram, still more preferably at least about 1.2 meq/gram. Cationic charge density of the cationic polymer can be determined according to the Kjeldahl Method. Those skilled in the art will recognize that the charge density of amino-containing polymers may vary depending upon pH and the isoelectric point of the amino groups. The charge density should be within the above limits at the pH of intended use.

Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g., CI, Br, I, or F, preferably CI, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C<sub>1</sub> - C<sub>7</sub> alkyl groups, more preferably C<sub>1</sub> - C<sub>3</sub> alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the composition. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably a  $C_1$  -  $C_7$  alkyl, more preferably a  $C_1$  -  $C_3$  alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate. monoalkylaminoalkyl acrylate. monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C1 - C3 alkyls, more preferably C<sub>1</sub> and C<sub>2</sub> alkyls. Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate. dialkylaminoalkyl and acrylamide, dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C1 - C7 hydrocarbyls, more preferably C<sub>1</sub> - C<sub>3</sub>, alkyls.

The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referr d to in the industry by CTFA as Polyquaternium-11) such as those commercially available

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from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include those of the formula:

wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual, R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>) preferably being about 20 or less, and X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR® and LR® series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200®.

Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially

available from Celanese Corp. in their Jaguar R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated herein by reference), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated herein by reference.)

#### Silicones

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Silicones useful herein are volatile soluble or insoluble, or nonvolatile soluble or insoluble. By "soluble" what is meant is that the silicones are miscible with water so as to form part of the same phase. By insoluble what is meant is that the silicones forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicones.

The nonvolatile dispersed silicones compounds useful herein will preferably have a viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from about 10,000 to about 1,800,000, and even more preferably from about 100,000 to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970, which is incorporated by reference herein in its entirety. Suitable silicone fluids include polyalkyl siloxanes, polyaryl siloxanes, polyaryl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other nonvolatile silicones having hair conditioning properties can also be used.

The nonvolatile dispersed silicones herein also include polyalkyl or polyaryl siloxanes with the following structure (I)

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wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and

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is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. polydimethylsiloxane, polydiethylsiloxane, preferred silicones are and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicones are available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

Polyalkylaryl siloxanes can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 METHYL PHENYL FLUID or from Dow Corning as 556 COSMETIC GRADE FLUID.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicones, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicones are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

The nonvolatile dispersed silicones that can be used include, for example, a polypropylene oxide modified polydimethylsiloxane although ethylene oxide or mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Other nonvolatile dispersed silicones include amino substituted materials. Suitable alkylamino substituted silicones include those represented by the following structure (II)

CH3 R

| HO - 
$$[Si-O]_x - [Si-O]_y - H$$
 (II)

5 CH3 (CH2)3
| NH
| (CH2)2
| NH2

wherein R is CH3 or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino substituted silicones include those represented by the formula (III)

$$(R^1)_a G_{3-a} - Si - (-OSiG_2)_n - (-OSiG_b(R^1)_{2-b)m} - O - SiG_{3-a}(R^1)_a$$
 (III)

in which G is chosen from the group consisting of hydrogen, phenyl, OH, C1-C8 20 alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R<sup>1</sup> is a monovalent radical 25 of formula CqH2qL in which q is an integer from 2 to 8 and L is chosen from the groups

$$-N(R^2)CH_2-CH_2-N(R^2)_2$$
  
30  $-N(R^2)_2$   
 $-N(R^2)_3A^-$   
 $-N(R^2)CH_2-CH_2-NR^2H_2A^-$ 

in which R<sup>2</sup> is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A denotes a halide ion.

An especially preferred amino substituted silicones corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):

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In this formula n and m are selected depending on the exact molecular weight of the compound desired.

Other amino substituted silicones which can be used are represented by the formula (V):

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where  $R^3$  denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl;  $R^4$  denotes a hydrocarbon radical, preferably a  $C_1-C_{18}$  alkylene radical or a  $C_1-C_{18}$ , and more preferably  $C_1-C_8$ , alkyleneoxy radical; Q is a halide, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

References disclosing suitable nonvolatile dispersed silicones include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to Drakoff, issued June 22, 1976; U.S. Patent No. 4,364,837, to Pader; and British Patent No. 849,433, to Woolston, all of which are incorporated herein by reference in their entirety. Also incorporated herein by reference in its entirety is "Silicon Compounds" distributed by Petrarch Systems, Inc., 1984. This reference provides an extensive, though not exclusive, listing of suitable silicones.

Another nonvolatile dispersed silicones that can be especially useful is a The term "silicone gum", as used herein, means a silicone gum. polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicones. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference in their entirety. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of trifunctional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl, dimethyl, trimethyl, monophenyl, diphenyl, methylphenyl, monovinyl, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile

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silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicones on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as Tospearl<sup>TM</sup> from Toshiba Silicones.

Background material on silicones, including sections discussing silicone fluids, gums, and resins, as well as the manufacture of silicones, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, which is incorporated herein by reference in its entirety.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit (CH<sub>3</sub>)<sub>3</sub>SiO) 5; D denotes the difunctional unit (CH<sub>3</sub>)<sub>2</sub>SiO; T denotes the trifunctional unit (CH<sub>3</sub>)SiO<sub>1.5</sub>; and Q denotes the quadri- or tetra-functional unit SiO2. Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to

about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

### **Proteins**

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Proteins useful herein include proteins derived from a natural source, and protein derivatives. Nonlimiting examples of proteins include hydrolysed collagen, hydrolysed keratin, and proteins.

Commercially available proteins useful herein include: materials having tradenames CROTEIN series available from Croda, and PROMOIS series available from Seiwa Kasei.

# 10 ADDITIONAL COMPONENTS

A wide variety of other additional components can be formulated into the present composition. These additional components are selected by the artisan according to the desired characteristics of the final product. Additional components include nonionic surfactants, amphoteric surfactants, zwitterionic surfactants; aqueous solvents such as C<sub>1-5</sub> alkyl monohydric alcohols and polyvinyl alcohol; oily solvents such as volatile and non-volatile silicone fluids of low molecular weight; thickening agents and suspending agents such as xanthan gum, guar gum, hydroxyethylcellulose, methylcellulose, starch and starch derivatives; viscosity modifiers such as methanolamides of long chain fatty acids such as cocomonoethanolamide; pearlescent aids such as ethylene glycol distearate; preservatives such as benzyl alcohol, methyl paraben, propyl paraben, imidazolidinyl urea, methylchloroisothiazoline, and methylisothiazoline; pH adjusting agents, such as sodium citrate, phosphoric acid, sodium hydroxide, and sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; sequestering agents such as ethylenediamine tetraacetate and its salts thereof; polymer plasticizing agents, such as glycerin, disobutyl adipate, butyl stearate, and propylene glycol; ultraviolet and infrared screening and absorbing agents such as octyl salicylate, antidandruff agents such as zinc pyridinethione, and propellants such as fluorohydrocarbons, dimethyl ether, carbon dioxide, nitrogen, and LPG gas. Such optional additional components generally are used individually at levels from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0% by weight of the composition.

#### METHOD OF MAKING

The hair conditioning compositions of the present invention are preferably made by a method comprising three steps. The first step comprises mixing water, the amidoamine, and a portion of the acid at a temperature of at least 70° C. The second step comprises addition of the high melting point compound to the obtained mixture while maintaining the temperature. Agitation usually accompanies the second step. The third step comprises cooling the obtained mixture to a temperature below 60°C, wherein the remaining acid, if any, is added. Then, the low melting point oily compound, and other components are added.

It has been discovered that, by changing the amount of acid included in the first step, compositions of various characteristics can be made. When from about 80% to about 100%, preferably 100% of the acid is included in the first step, a conditioning composition which provides relatively more shear-thinning property is obtained. This rheology can be recognized by the consumer as good spreadability and good rinsability. When from about up to 80%, preferably from about 50% to about 75% of the acid is included in the first step and the remainder included in the third step, a conditioning composition which provides relatively less shear-thinning property is obtained. This rheology can be recognized by the consumer as richness, and creaminess.

The amount of acid to include in the first step, therefore, is determined in view of the components used in the composition according to the desired benefits of the final product.

#### **EXAMPLES**

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, since many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

The hair conditioning ingredients herein are expressed by weight percentage of the total compositions, unless otherwise specified.

### **EXAMPLES I-IV**

These examples show hair rinse compositions of the present invention and the method of making thereof.

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	Component (Wt.%)	Ex.I	Ex.II	Ex.III	Ex.IV
	Stearamidopropyldimethylamine $^{\star 1}$	2.00	1.60	2.00	1.60
	L-Glutamic Acid <sup>*2</sup>	0.64	0.51	0.64	0.51
	Cetyl Alcohol <sup>*3</sup>	2.50	2.00	2.50	5.60
5	Stearyl Alcohol <sup>*4</sup>	4.50	3.60	4.50	
	Oleyl Alcohol <sup>*5</sup>	0.25	0.20	0.58	0.20
	Mineral Oil*6	0.25	0.20	0.58	0.20
	Silicones <sup>*7</sup>	4.20	3.36	4.20	3.36
	Benzyl Alcohol	0.40	0.40	0.40	0.40
10	EDTA	0.10	0.10	0.10	0.10
	Kathon CG <sup>*8</sup>	0.03	0.03	0.03	0.03
•	Sodium Chloride		0.01		0.01
	Perfume	0.20	0.20	0.20	0.20
	Water	84.93	87.79	84.27	87.79

For Examples I through IV, water, stearamidopropyldimethylamine and about 50% of L-glutamic acid are mixed at a temperature above 70°C. Then th high melting point fatty compounds and benzyl alcohol are added with agitation. After cooling down below 60°C, the remaining L-glutamic acid and other remaining components are added with agitation, then cooled down to about 30°C.

Examples I through IV have many advantages. For example, they can provide richness and creaminess to the wet hair, and also show good combing feel and lustery appearance when the hair is dry.

#### **EXAMPLES V - VIII**

Examples V through VIII are hair rinse compositions having the same compositions as disclosed above for Examples I through IV, respectively, made with the following method.

Water, stearamidopropyldimethylamine and all of L-glutamic acid ar mixed at a temperature above 70°C. Then the high melting point fatty compounds and benzyl alcohol are added with agitation. After cooling down below 60°C, the remaining components are added with agitation, then cooled down to about 30°C.

Examples V through VIII have many advantages. For example, they can provide good spreadability and good rinsability when the wet hair, and also show good combing feel and lustery appearance when the hair is dry.

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# **EXAMPLES IX - XII**

These examples show hair rinse compositions of the present invention and the method of making thereof.

Ex.IX	Ex.X	Ex.XI	Ex.XII
2.00	2.00		<del>-</del> -
		2.00	2.00
0.64	0.64	0.64	0.64
7.00		7.00	7.00
	7.00		
0.25	0.58	0.25	0.20
0.25	0.58	0.25	0.40
4.20	4.20	4.20	2.00
	0.40		
0.20		0.20	0.20
0.10		0.10	0.10
0.10	0.10		0.10
0.03	0.03	0.03	0.03
0.20	0.20	0.20	0.20
85.03	84.27	85.13	87.13
	2.00  0.64 7.00  0.25 0.25 4.20  0.20 0.10 0.10 0.03	2.00 2.00 0.64 0.64 7.00 7.00 0.25 0.58 0.25 0.58 4.20 4.20 0.40 0.20 0.10 0.10 0.03 0.03 0.20 0.20	2.00 2.00 2.00 0.64 0.64 0.64 7.00 7.00 7.00 0.25 0.58 0.25 0.25 0.58 0.25 4.20 4.20 4.20 0.40 0.20 0.20 0.10 0.10 0.10 0.10 0.03 0.03 0.03 0.20 0.20 0.20

For Examples IX through XII, water, the amidoamine and 50% of L-glutamic acid are mixed at a temperature above 70°C. Then the high melting point fatty compounds and benzyl alcohol, if applicable, are added with agitation. After cooling down below 60°C, the remaining 50% of L-glutamic acid and remaining components are added with agitation, then cooled down to about 30°C.

Examples IX through XII have many advantages. For example, they can provide richness and creaminess to the wet hair, and also show good combing feel and lustery appearance when the hair is dry.

#### **EXAMPLES XIII - XVI**

Examples XIII through XVI are hair rinse compositions having the same compositions as disclosed above for Examples IX through XII, respectively, made with the following method.

Water, the amidoamine and all of L-glutamic acid are mixed at a temperature abov 70°C. Then the high melting point fatty compounds and benzyl alcohol are added with agitation. After cooling down below 60°C, the

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remaining components are added with agitation, then cooled down to about 30°C.

Examples XIII through XVI have many advantages. For example, they can provide good spreadability and good rinsability when the wet hair, and also show good combing feel and lustery appearance when the hair is dry.

#### **Definitions**

- <sup>\*1</sup> Stearamidopropyldimethylamine: AMIDOAMINE MPS obtained by Nikko
- L-glutamic acid: L-GLUTAMIC ACID (cosmetic grade) obtained by Ajinomoto
- 10 \*3 Cetyl Alcohol: KONOL series obtained by New Japan Chemical
  - <sup>\*4</sup> Stearyl Alcohol: KONOL series obtained by New Japan Chemical
  - \*5 Oleyl Alcohol: UNJECOL 90BHR obtained by New Japan Chemical
  - \*6 Mineral Oil: BENOL obtained by Witco
- Silicones: 85%/15% (weight base) mixture of D5 Cyclomethicone and dimethicone gum (weight average molecular weight of about 400,000 to about 600,000) obtained by General Electric Co.
  - \*8 Kathon CG: Mixture of methylchloroisothiazoline and methylisothiazoline obtained by Rohm & Haas Co., (Philadelphia, PA, USA).
  - \*9 Stearamidoethyldiethylamine: AMIDOAMINE S obtained by Nikko

#### .WHAT IS CLAIMED IS:

- 1. A hair conditioning composition comprising by weight:
- (a) from about 0.4% to about 5.0% of an amidoamine having the following general formula:

R1 CONH (CH2)m N (R2)2

- wherein R<sup>1</sup> is a fatty acid residue having from about 11 to about 24 carbon atoms, R<sup>2</sup> is an alkyl having from 1 to about 4 carbon atoms, and m is an integer from 1 to about 4;
  - (b) from about 0.05% to about 2.0% of an acid;
- (c) from about 1% to about 15% of a high melting point compound having a melting point of at least about 25°C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof;
  - (d) from about 0.02% to about 2% of an oily compound having a melting point of not more than about 25°C selected from the group consisting of a first oily compound, a second oily compound, and mixtures thereof; and
  - (e) water;

wherein the molar ratio of the amidoamine to the acid is from about 1:0.3 to about 1:1, and wherein the composition is substantially free of quaternary ammonium compounds.

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- 2. The hair conditioning composition according to Claim 1 comprising by weight:
- (a) from about 1.0% to about 3.0% of the amidoamine;
- (b) from about 0.3% to about 1.0% of the acid;
- 5 (c) from about 3% to about 8% of the high melting point compound;
  - (d) from about 0.2% to about 1.5% of the oily compound; and
  - (e) water;
  - 3. The hair conditioning composition according to Claim 2 comprising by weight:
  - (d1) from about 0.1 to about 0.75% of the first oily compound; and
  - (d2) from about 0.1 to about 0.75% of the second oily compound.

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4. The hair conditioning composition according to Claim 3 wherein the first oily compound is selected from the group consisting of oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isostearyl alcohol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol, decyl alcohol, lauryl alcohol, and mixtures thereof.

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- 5. The hair conditioning composition according to Claim 3 wherein the second oily compound is selected from the group consisting of mineral oil, isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.
- 6. The hair conditioning composition according to Claim 3 further comprising an additional conditioning agent selected from the group consisting of cationic polymers, silicones, proteins, and mixtures thereof.
- 7. The hair conditioning composition according to any of Claims 1 through 6 wherein the amidoamine is selected from the group consisting of stearamidopropyldimethylamine, stearamidoethyldiethylamine, and mixtures thereof.

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8. The hair conditioning composition according to any of Claims 1 through 6 wherein the acid is selected from the group consisting of L-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, L-glutamic acid hydrochloride, tartaric acid, and mixtures thereof.

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9. The hair conditioning composition according to any of Claims 1 through 6 wherein the high melting point compound is selected from the group consisting of straight chain saturated fatty alcohols having 16 to 22 carbon atoms and mixtures thereof.

- 10. The hair conditioning composition according to any of Claims 1 through 6 wherein the high melting point compound is selected from the group consisting of pure cetyl alcohol, pure stearyl alcohol, and pure behenyl alcohol.
- 11. A method of making the hair conditioning composition according to any of Claims 1 through 6 comprising the steps of:

- (a) mixing the amidoamine, not more than about 80% of the acid, and water at a temperature of above 70°C;
- 5 (b) adding the high melting point compound to the product of (a) at a temperature of above 70°C; and
  - (c) cooling the product of (b) to a temperature of below 60°C and adding the remainder of the acid.
  - 12. A method of making the hair conditioning composition according to any of Claims 1 through 6 comprising the steps of:
  - (a) mixing the amidoamine, from about 80% to about 100% of the acid, and water at a temperature of above 70°C;
- 5 (b) adding the high melting point compound to the product of (a) at a temperature of above 70°C; and
  - (c) cooling the product of (b) to a temperature of below 60°C and adding the remainder of the acid.

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# INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : A61K 7/06	A3	<ul> <li>(11) International Publication Number: WO 98/40046</li> <li>(43) International Publication Date: 17 September 1998 (17.09.98)</li> </ul>
(21) International Application Number: PCT/US (22) International Filing Date: 10 March 1997 ( (71) Applicant (for all designated States except US): THE TER & GAMBLE COMPANY [US/US]; One Foundle Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MITSUMATS [JP.JP]: 7-33-203, Asahigaoka-cho, Ashiya, Hy (JP). NAKAMURA, Kiichiro [JP/JP]; 1-10-1 Koyo-cho Naka, Higashinada-ku, Kobe 658 (JP). (74) Agents: REED, T., David et al.; The Procter & Company, 5299 Spring Grove Avenue, Cincin 45217 (US).	E PROProcter SU, Arayogo 6: 01–271	BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TI UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAP patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE SN, TD, TG).  Published  With international search report.

#### (57) Abstract

Disclosed are hair conditioning compositions comprising by weight: (a) from about 0.4 % to about 5.0 % of an amidoamine; (b) from about 0.05 % to about 2.0 % of an acid; (c) from about 1 % to about 15 % of a high melting point compound having a melting point of at least about 25° C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof; (d) from about 0.02 % to about 2 % of an oily compound having a melting point of not more than about 25° C selected from the group consisting of a first oily compound, a second oily compound, and mixtures thereof; and (e) water; wherein the molar ratio of the amidoamine to acid is about 1: 0.3 to about 1: 1, and wherein the composition is substantially free of quaternary ammonium compounds. Further disclosed are suitable methods of making the conditioning compositions.

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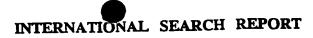
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C. DOCUME	ENTS CONSIDERED TO BE RELEVANT		
Category ;	Citation of document, with indication, where appropriate, of the rele	vant passages	Relevant to claim No.
A	DE 42 32 506 A (HENKEL) 31 March see examples B1-B11,1-2	1994	1-12
A	STN File Supplier, Karlsruhe, DE, XP002046285 Chemical Abstracts, vol 113, AN=2 see the abstract & JP 02 160 714 A (KANEBO)		1-12
Α	WO 95 20939 A (PROCTER & GAMBLE) 1995 see the whole document	10 August	1-12
А	EP 0 562 639 A (HELENE CURTIS) 29 September 1993 see the whole document		1-12
Furti	ner documents are listed in the continuation of box C.	χ Patent family members are listed in	n annex.
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Information on patent family members

Int. .ational Application No PCT/US 97/03564

Patent document cited in search repo	1	Publication date	Patent family member(s)			Publication date	
DE 4232506	A 31	-03-94	DE 5	147617 147258 2145860 2145861 1085775 1089135 59303272 59305092 59305172 9407455 9407458 0662814 0662815 0662816 2091015	A A D D D A A A A A A T T T A	15-08-96 15-02-97 15-01-97 14-04-94 14-04-94 27-04-94 13-07-94 22-08-96 20-02-97 27-02-97 14-04-94 14-04-94 14-04-94 19-07-95 19-07-95 19-07-95 16-10-96 16-03-97 18-06-96 30-06-94 31-03-94	
WO 9520939	A 10	0-08-95 	AU EP	1606995 0743846		21-08-95 27-11-96	
EP 562639	A 29	9-09-93	US AU CA JP MX NZ US US ZA	5393519 3526793 2091872 6009351 9300690 247246 5587154 5665267 9301612	A A A A A A	28-02-95 30-09-93 28-09-93 18-01-94 01-09-93 27-04-95 24-12-96 09-09-97 21-06-94	